

EMRP 2009 ENG09 (Biofuels) – WP3

Report

Deliverable 3.2b Comparison measurements to assess comparability and generate exemplar reference data for conductivity

Responsible Institute: DFM
Collaborating Institutes: PTB, INRiM

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Summary

Comparison measurements of electrolytic conductivity of bioethanol and synthetic ethanol samples have been performed by three national metrology institutes (PTB, INRiM, DFM). The comparisons mainly served as an assessment of sample preparation, measurement procedures, data evaluation and compatibility of measurement results. Homogeneity measurements of conductivity showed an empirical standard deviation of 0.7 % for bioethanol and 24 % for synthetic ethanol at values in the range of roughly $180 \mu\text{S m}^{-1}$ (bioethanol) and $2 \mu\text{S m}^{-1}$ (synthetic ethanol). The values of the reported results and their distribution are in the same range as the homogeneity results. However, sample homogeneity is not necessarily as poor as it seems, since all institutes reported problems with repeatability, in particular with respect to synthetic ethanol. After some possible improvements, mainly with respect to sample preparation and an increased number of measurements in order to get a more sound data base, a conductivity reference values for bioethanol with a relative standard uncertainty around 0.1 % seems achievable. The relative uncertainty of a reference conductivity value for synthetic ethanol can probably not be decreased. However, the absolute uncertainty is small compared to the conductivity value of bioethanol. A reference conductivity value for synthetic ethanol therefore can nevertheless reliably serve to assess the degree of ionic contamination of bioethanol by conductivity measurements. Due to the results no reference values have been calculated. It is recommended to repeat the comparison measurements in the last year of the project.

Background

Electrical characterization is an area of interest in terms of the identification of trace impurities levels within biofuels. High measurement accuracy, and a stringent application of metrological principles in establishing traceability for these measurements, is mandatory to achieve reliable results. In particular, research into the electrolytic conductivity as 'quality indicator' for biofuels is necessary to assess risk of corrosion and potential damage to engines. Essential work is still required to underpin the traceability of the results for conductivity as quality indicator.

To this end the comparison measurement at present has been introduced as deliverable 3.2b into ENG09-WP3 activities. It has been conducted under the umbrella of an EURAMET study (# 1202). The aim of the comparison is a first verification of the equivalence of electrolytic conductivity results, measured on samples of synthetic ethanol and bioethanol. Particularly, in this way it is tested, if sample preparation and handling are appropriate to achieve compatible measurement results.

Preliminary results have shown that the conductivities measured in bioethanol from different origins are significantly different. The conductivity of synthetic ethanol therefore seemed to be a more suitable reference in order to assess the contribution of ionic contaminants to the conductivity of bioethanol. Therefore, additionally those of bioethanol, the results obtained in synthetic ethanol are compared.

Sample characterisation

Two solutions have been provided by the Physikalisch-Technische Bundesanstalt (PTB): bioethanol and synthetic ethanol (Merck 1.00983.2511, 99.9%). The samples of each solution were prepared in the following way. The ethanol was filled into a 2 L bottle, than the bottle was closed and homogenized. Afterwards the lid was removed and the open was closed with a film. A tube was inserted through the film into the bottle. The solution was sucked in and around 200 mL of solution was discarded. Then it was filled into 250 mL borosilicate glass bottles until the solution brimmed over. Then 20 mL of solution was sucked out again, using a syringe, before the bottle was closed with a lid. The complete procedure was performed as fast as possible to keep contact time of the solution with atmosphere short. Then the masses of bottles were measured. The bottles were labelled with a bottle number, the production date and a nominal value of conductivity. Each participant has received two bottles of bioethanol sample and two bottles of synthetic ethanol. Shipment to all the participating laboratories is performed at the same time, and the comparison measurements are to be performed in parallel. The two bottles, one from each batch, are shipped in one cardboard box by courier.

Before shipment, the coordinating laboratory performed secondary measurements on three bottles to verify the homogeneity of the batch. The results are shown in figure 1. The means/ the empirical standard deviations and the relative standard deviations are:

$$\begin{aligned} &181.04 \mu\text{S m}^{-1} / 2.1 \mu\text{S m}^{-1} / 0.7\% \text{ (bioethanol)} \\ &1.97 \mu\text{S m}^{-1} / 0.4 \mu\text{S m}^{-1} / 24\% \text{ (synthetic ethanol)}. \end{aligned}$$

Concerning bioethanol, if only bottles 10, 11 and 12 are considered, the relative standard deviation would be 0.1 %, which is a sufficiently low spread. However, the result of bottle 1 suggests that there might be outliers among the samples. The relative standard deviation of the conductivity values of synthetic ethanol is rather large, suggesting a poor homogeneity.

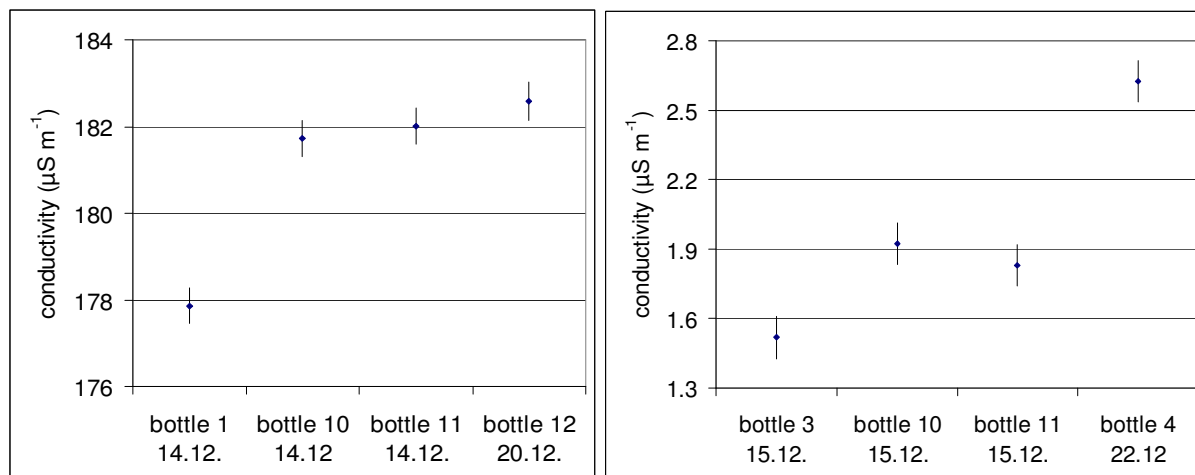


Figure 1 Measured conductivity values of samples measured at the PTB to estimate the homogeneity of the samples. Left: bioethanol, right synthetic ethanol. The error bars indicate the expanded ($k=2$) uncertainty. The date on the x-axis indicates the date of the measurement.

However, the spread of the absolute values is still smaller than that of bioethanol. It cannot be excluded that the measurement uncertainty is underestimated and that the spread of the results is rather due to poor repeatability of the measurement results than to inhomogeneous samples.

The coordinating laboratory also measured conductivities at (nominal) 24.8 °C, 25 °C and 25.2 °C. The results are shown in figure 2. For bioethanol a linear temperature coefficient of 1.2 %/K (at 25 °C) was estimated. Since conductivity is typically corrected just about a few tens of mK to the set temperature no uncertainty has been attributed to the temperature coefficient. The measurement results of synthetic ethanol were superimposed by a linear drift of the conductivity value. After correcting the results for the drift, no dependence on temperature could be observed. However, it is more likely that the poor repeatability impedes the determination of the temperature coefficient than inferring that the conductivity of synthetic ethanol doesn't depend on temperature.

It should be noted that just a small number of samples were available for this first comparison, which explains the little number of measurements to characterise them.

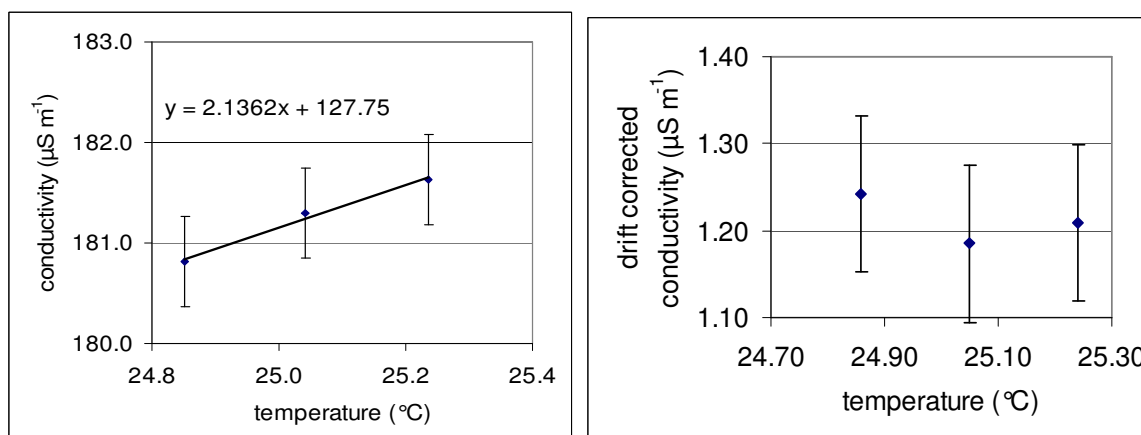


Figure 2 Conductivity values of bioethanol measured in dependence of temperature to estimate the temperature coefficient for bioethanol.

Actions before measurement

The bottles have been inspected for damage, leakage or visible deposits in the solution. Then they have been weighed (corrected for air buoyancy) and the mass values have been compared (within 0.2 g) with the values that had been measured at the coordinating laboratory before. INRiM received a new bottle, since one of the originally sent bottles was leaking. No further peculiarities have been reported by the labs.

Before the measurement the bottles were stored at room temperature for at least two days. All participants performed the measurements in the same week to reduce any influence on the conductivity measurements results that might be caused by instable samples. The temperature of the samples was adjusted to the measurement temperature before it was filled into the measuring cell in order to keep the time between uncapping of the bottle and the achievement of the set temperature in the measuring cell short. Finally, the bottles have been carefully turned upside-down several times to homogenize the solution before it was filled in the cell (without shaking to avoid bubble formation).

Measurement results

Bioethanol referred to 25 °C

Lab.	t1 (min)	t2 (min)	Drift (% h ⁻¹)	method	conductivity ($\mu\text{S m}^{-1}$)	stand. uncert. ($\mu\text{S m}^{-1}$)	traceability remarks
PTB	<1	86	non	secondary cell	182.58	0.22	calibration with $130\mu\text{S m}^{-1}$ KCl(glyc) traceable to SI by primary measurement at PTB
INRiM	<3	0	0.016 (i)	secondary cell	184.5	1.99	calibration with 1mS m^{-1} KCl(aqu) traceable to SI by primary measurement at INRiM
DFM	<1	0	non	secondary cell	162.56	0.09 (only stddev)	calibration with $130\mu\text{S m}^{-1}$ KCl(glyc) traceable to SI by primary measurement at DFM

t1 time sample was exposed to air before filling

t2 time the measurement result is related to with respect to filling of the cell

(i) INRiM observed a change of $0.0289 \mu\text{S m}^{-1}$ in 10 hours measurement time, attributed to pollution

Lab.	meas. temp. (° C)	temp. correct.	set voltage (V)	frequ. range (kHz)	determination of solution bulk resistance
PTB	25.065	yes	0.5	10-400	fit of semi circle into high frequency arc of spectrum
INRiM	close to 25	yes	0.5		Real(Z_{\min}), with Z_{\min} is impedance with minimum reactance
DFM	25.000	no	0.5	0.02-0.3	extrapolation of $1/\text{Real}(Y)$ versus $1/f \rightarrow 0$, (Y Admittance, f frequency)

Synthetic ethanol referred to 25 °C

Lab.	t1	t2	Drift	method	conductivity	stand. uncert.	traceability
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	(min)	(min)	(% h ⁻¹)		($\mu\text{S m}^{-1}$)	($\mu\text{S m}^{-1}$)	remarks
PTB	<1	0 (i)	3.4	secondary cell	2.62	0.09	calibration with $130\mu\text{S m}^{-1}$ KCl(glyc) traceable to SI by primary measurement at PTB
INRiM	<3	0	1.3(ii)	secondary cell	2.27	0.04	calibration with 1mS m^{-1} KCl(aqu) traceable to SI by primary measurement at INRiM
	<3	0	1.1(ii)		2.74	0.044	
DFM	<1	20	0.6	tertiary cell	2.219	0.015 (only stddev)	calibration with $130\mu\text{S m}^{-1}$ KCl(glyc) traceable to SI by primary measurement at DFM

- (i) conductivity value linearly extrapolated (6 measurements in 4h) to the time of cell filling to correct for linear drift
(ii) INRiM observed a change of $0.0289 \mu\text{S m}^{-1}$ in 10 hours measurement time, attributed to pollution

Lab.	meas. temp. (° C)	temp. correct.	set voltage (V)	frequ. range (kHz)	determination of solution bulk resistance
PTB	25.039	no	0.5	10-400	fit of semi circle into high frequency arc of spectrum
INRiM	close to 25	no	0.5	20-1000	Real(Z_{\min}), with Z_{\min} is impedance with minimum reactance
DFM	25.000	no	0.5	0.02-0.3	extrapolation of $1/\text{Real}(Y)$ versus $1/f \rightarrow 0$, (Y Admittance, f frequency)

Conclusions

All institutes have made the experience that the repeatability of measurement results of synthetic ethanol is relatively poor. Hence, it can not be assessed if the large spread of the reported results is due to poor repeatability, due to inhomogeneous samples as one could suggest from figure 1, or due to differences in the measurement and data evaluation procedures. However, the purpose of measuring synthetic ethanol was to get a reference conductivity value to assess the contamination of bioethanol by conductivity measurements. Even though the mean of the reported values ($2.46 \mu\text{S m}^{-1}$) has a large relative uncertainty of around 10% (taking the empirical standard deviation as an uncertainty measure) it still can serve as an estimate for this purpose, since the absolute uncertainty of about $0.2 \mu\text{S m}^{-1}$ to $0.3 \mu\text{S m}^{-1}$ is relatively small compared to the conductivity values of bioethanol.

The deviation of the bioethanol conductivity value reported by DFM is significant. It can neither be explained by the measurement uncertainties, nor by the homogeneity limits shown in figure 1 (left). DFM and PTB used equal calibration solutions, which were calibrated using their primary calibration procedures. In CCQM pilot study P83 (using a similar solution) it was demonstrated that these lead to compatible results. Moreover, the resistance measurement in a cell calibration and in the subsequent bioethanol measurement are strongly correlated. So even if the determination of the solution bulk resistance shows a systematic error with respect to the (true) SI value, meaning the resistances measured by DFM and PTB are not comparable (in the metrological sense), this error should cancel for the most part, when conductivity is calculated with respect to the conductivity value of the calibration solution. Therefore the large difference in the bioethanol conductivity values can not be understood easily. This could only be explained if the differences in the current pathway, due to differences in the electric field distribution, for bioethanol and the calibration solution deviate significantly in the cells used. However, both cell geometries are such, that the pathways are mostly restricted to the volume between the electrodes. Here, difference in the current path in one solution compared to another can only occur at the rims of the volume and therefore only contribute weakly to the measured solution bulk resistance. Hence, it is not very likely that this can explain the deviation. So other possible reasons must be discussed.

Meanwhile the sample preparation procedure for bioethanol has been improved, such that a standard deviation of less than 0.1 % could be achieved in a homogeneity test with five samples. The foil, which seals the bottle used to homogenise the sample, has been replaced by a lid with two ports. The filling is done under Argon atmosphere and a larger amount of solution is discarded at the beginning.

The compatibility of the results is too poor to allow calculating a useful reference values in the metrological sense (i.e. to calculate degrees of equivalence). The reference value given above for synthetic ethanol is, as mentioned, meant as a reference point to estimate the ionic contamination of bioethanol from conductivity measurements. However, from the experience made in this comparison and from further follow-up measurements at the PTB one can assume that a better compatibility is achievable.

Therefore it is proposed to repeat the comparison measurement in the last year of the project, including the following improvements:

- Use of improved preparation procedure.
- Filling of the cell under Argon atmosphere, that is saturated with ethanol.
- Performance of characterisation measurements with at least five samples.
- Determination of the temperature coefficients using a wider temperature range.
- Each institute should at least measure three samples from the three bottles.

- Each institute should report at least 5 measurement results, measured within a period of at least 4 hours to demonstrate the drift.
- All participants should use the same calibration solution, preferably the $130 \mu\text{S m}^{-1}$ KCl(glyc) solution, since its value is closer to that of bioethanol.
- The number of participants should be increased.